

CLEERS: Aftertreatment Modeling and Analysis

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Pacific Northwest National Lab
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ACE023

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Overview

► Timeline

- Status: On-going core R&D
- DPF activity originated in FY03
- Now also includes LNT, SCR and DOC technologies

► Budget

- FY12 funding - \$750K
- FY13 funding (thru 3/13) - \$123K
 - SCR task – primary
 - LNT task – minor (~\$15k)
 - DPF task – secondary (delayed)



► Barriers

- Emission controls contribute to durability, cost and fuel penalties
 - Low-temp performance of particular concern
- Improvements limited by:
 - available modeling tools
 - chemistry fundamentals
 - knowledge of material behavior
- Effective dissemination of information

► Partners

- DOE Advanced Engine Crosscut Team
- CLEERS Focus Group
- 21CTP partners
- USCAR/USDRIIVE ACEC team
- Oak Ridge National Lab

Goal and Relevance

- ▶ “CLEERS is a R&D focus project of the Diesel Cross-Cut Team. The overall objective is to promote development of improved computational tools for simulating realistic full-system performance of lean-burn engines and the associated emissions control systems.”

CLEERS PNNL Subprogram Goal

Working closely with our National Lab partners, the CLEERS industrial/academic team and in coordination with our CRADA portfolio, PNNL will...

...provide the practical & scientific understanding and analytical base required to enable the development of efficient, commercially viable emissions control solutions and modeling tools for ultra high efficiency vehicles.

- ▶ VT program goals are achieved through these project objectives:
 - interact with technical community to indentify relevant technological gaps
 - understand fundamental underlying mechanisms and material behavior
 - develop analytical and modeling tools, methodologies, and best practices
 - apply knowledge and tools to advance technologies leading to reducing vehicle emissions while improving efficiency
- ▶ Specific work tasks in support of the objectives are arrived at through:
 - focus group industrial monthly teleconferences, diesel X-cut meetings
 - yearly workshops and surveys
 - Ongoing discussions on program priorities with the VT office

Technical Milestones & Approach

- ▶ The overall performance measure of the project is inextricably linked to the interests of industry
 - PNNL CLEERS activities have resulted in the formation of new CRADAs
 - Tremendous success of the annual workshops
 - Strong participation in the monthly teleconferences

- ▶ Specific performance measures are developed with the industrial/academic partners and captured in SOW
 - Specific technical targets and major milestones are described in our AOPs and annual reports to VT

- ▶ Approach - “Science to Solutions”
 - We build off of our strong base in fundamental sciences and academic collaborations
 - Institute for Integrated Catalysis (IIC)
 - Environmental Molecular Sciences Laboratory (EMSL)
 - With a strong pull towards industrial applications and commercialization
 - OEMs
 - TIER 1 suppliers
 - Working closely with our partners and sponsors
 - ORNL (coordination of website, workshops, etc.)
 - DOE Advanced Engine Cross-Cut Team

PNNL FY13 Portfolio

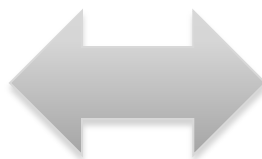
CLEERS activity

Integrated Systems – George Muntean

- DPF subtasks* – Mark Stewart
- SCR subtasks* – George Muntean
- LNT subtasks – Chuck Peden

*PNNL-led subteam

**Past activities



CRADA activities

DPF – DOW Automotive (Stewart)**

Fuel Neutral Particulate study (Stewart)

SCR/DPF – PACCAR (Rappe)

SCR/DPF – Ford Motor Company (Peden)

Low T Oxidation – General Motors (Peden)

SCR Dosing Systems – GM & Ford (Autrey)

SCR and LNT – Cummins Inc. (Peden)

Oxidation Catalysts**

– General Motors (Herling)

– SDC Materials (Herling)

– Caterpillar (Rappe)

FY2012/2013 Scope Objectives

► Selective Catalytic Reduction (SCR)

- Use data gathered with the CLEERS SCR transient protocol data at ORNL with current commercial Cu-CHA catalysts at various aging states to develop improved models
- Continue detailed kinetic and mechanistic studies for NO reduction over the state-of-the-art small-pore SSZ-13-based Cu SCR catalysts, including characterization measurements that probe the nature of the active Cu species.
 - Some focus on acidic properties as probed by ammonia TPD to support modeling efforts.
- Prepare model Cu-SAPO-34 CHA-zeolite based SCR catalysts for fundamental studies of their structure and reactivity.

► NO_x Storage-Reduction (NSR) Catalysts

- Determine mechanisms of precious-metal sintering resistance for MgAl₂O₄-based NSRs.
- Explore the use of titania supports for K-based NSRs (prior literature suggests special properties for these support materials).

► Particulate Filter (PF)

- Seek to identify key length scales and pore features associated with backpressure and filtration performance and examine how they are altered by catalyst coatings in multi-function filter devices
- Conduct cooperative experiments at ORNL to help characterize particulates from an advanced lean-burn gasoline direct injected vehicle

Technical Accomplishments Outline

► SCR

- Developed a two-site NH_3 storage and SCR reaction model
- Began incorporation of modeling features to describe performance changes of SCR catalysts over the course of their design life
- Structure, reactivity, and chemical properties (NH_3 storage) as a function of Cu loading in state-of-the-art Cu-SSZ-13 catalysts were determined. Kinetic studies on these materials shown to be complicated by mass transfer limitations.
- Potentially significant reaction intermediate for SCR on CHA-based catalysts identified.
- Explored the optimum preparation of model SAPO-34 CHA catalysts, including methods to incorporate Cu.

► NSR

- Studied the mechanisms of Pt-sintering resistance on magnesium aluminate supports that have been shown to significantly improve the NO_x reduction performance at high temperatures.
- Performed systematic studies of K loading effects on NO_x storage performance and deactivation of titania-supported NSR catalysts.

► PF

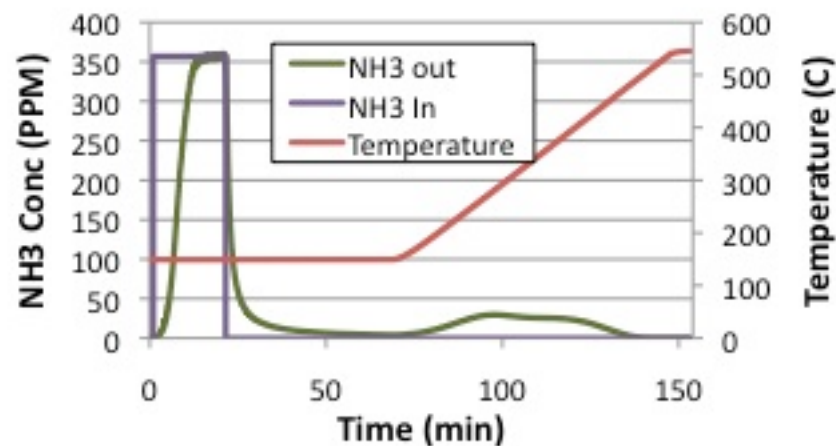
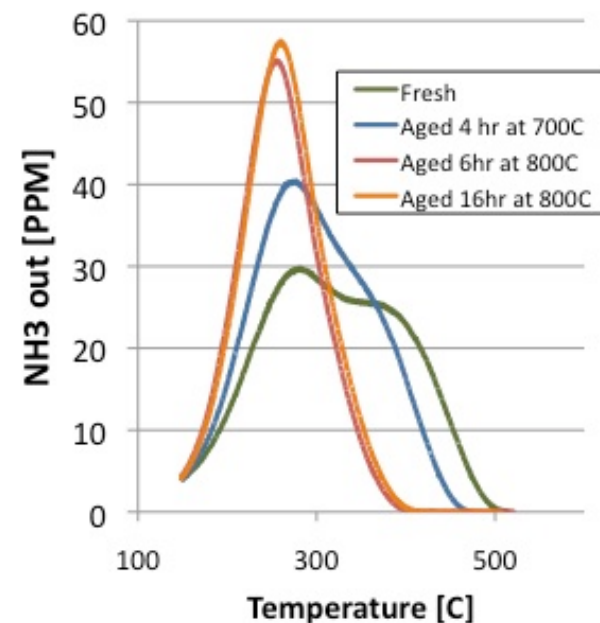
- High resolution three dimensional micro-CT images have been obtained for a current high-porosity filter substrate professionally coated with various loadings of a state-of-the-art SCR catalyst

Selective Catalytic Reduction

- modeling studies
 - overall goal is to develop catalyst aging factors, essential for model based control adaptation, using 1D SCR models.
 - transient protocol and TPD data collected on Cu-CHA samples at ORNL were used to develop the SCR model.
- materials characterization
 - characterization data of Cu-zeolite
 - hydrothermal deactivation

SCR Model using Two NH_3 Storage Sites

- Cooperative effort with ORNL
- ORNL kinetics experiments with current Cu-CHA SCR catalyst using TPD and the CLEERS transient SCR protocol
- TPD experiments with fresh and hydrothermally aged samples suggest two types of NH_3 storage sites
- “Fresh” catalyst was taken from an actual new vehicle
- During hydrothermal aging (intended to mimic aging during useful life) capacity seems to shift from one type of site the other
- A two site model was developed to describe observed changes in performance



Two Site NH₃ Storage Model

$$\frac{\partial c_{g,NH_3}}{\partial t} = -\frac{u}{\varepsilon} \frac{\partial c_{g,NH_3}}{\partial x} + \frac{\Omega_1}{\varepsilon} (r_{des,s1} - r_{ads,s1}) + \frac{\Omega_2}{\varepsilon} (r_{des,s2} - r_{ads,s2})$$

$$\frac{d\theta_{NH_3,1}}{dt} = r_{ads,s1} - r_{des,s1}$$

$$\frac{d\theta_{NH_3,2}}{dt} = r_{ads,s2} - r_{des,s2}$$

Form of storage model taken from Colombo et al, 2012

Site 1 (Weakly Adsorbed)

$$r_{ads,s1} = A_{ads,s1} C_{g,NH_3} (1 - \theta_{NH_3,s1})$$

$$r_{des,s1} = A_{des,s1} e^{\frac{-E_{des,s1}(1-\theta_{NH_3,s1})}{RT}} \theta_{NH_3,s1}$$

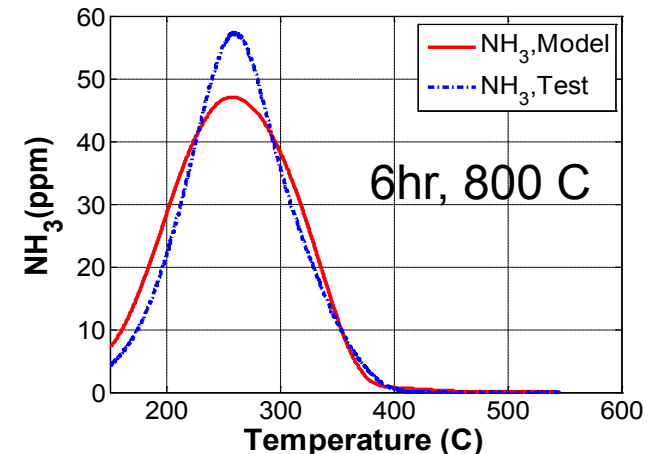
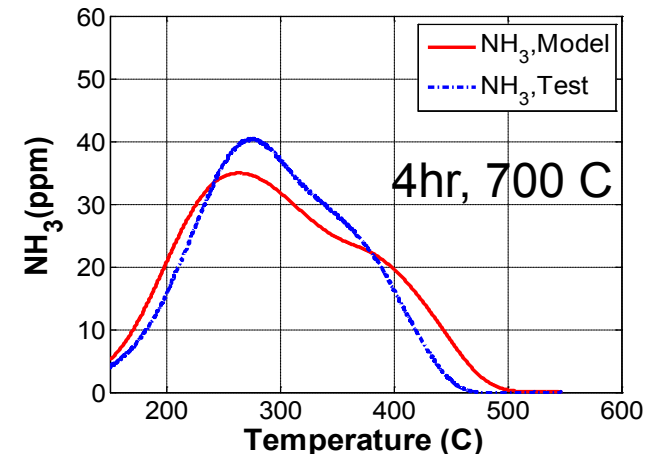
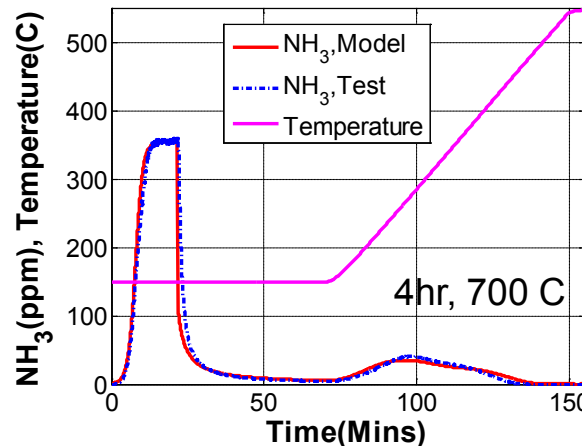
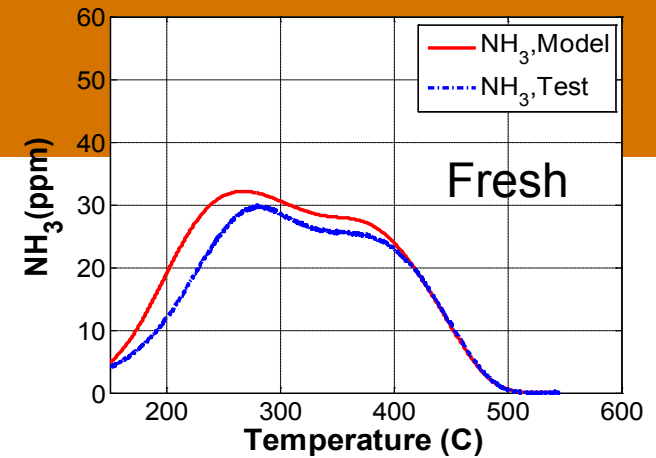
Site 2 (Strongly Adsorbed)

$$r_{ads,s2} = A_{ads,s2} C_{g,NH_3} (1 - \theta_{NH_3,s2})$$

$$r_{des,s2} = A_{des,s2} e^{\frac{-E_{des,s2}}{RT}} \theta_{NH_3,s2}$$

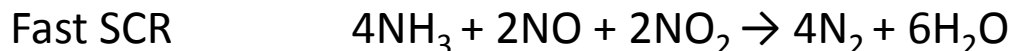
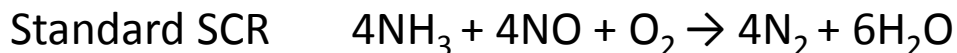
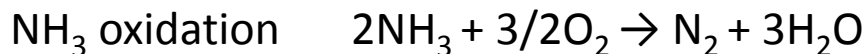
- ▶ Kinetic parameters for adsorption and desorption tuned to describe fresh and aged data
- ▶ Capacity associated with type 2 site is shifted to type 1 site during aging

Colombo, M., G. Koltsakis, I. Nova, and E. Tronconi, "Modelling the ammonia adsorption-desorption process over an Fe-zeolite catalyst for SCR automotive applications". *Catalysis Today*, 2012. 188(1): p. 42-52 DOI: 10.1016/j.cattod.2011.09.002.



Modeling Reactions Relevant to SCR

- ▶ Two-site kinetic models were also developed for various reactions which determine SCR performance
- ▶ All are keyed to the same changing distribution between the two site types proposed to describe storage experiments
- ▶ Values of kinetic parameters for the two sites are kept the same for all aging states – only the proportions of the two sites change

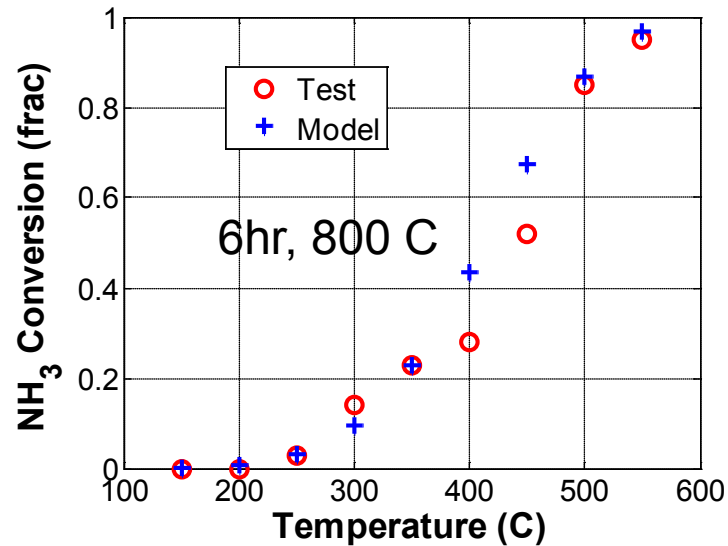
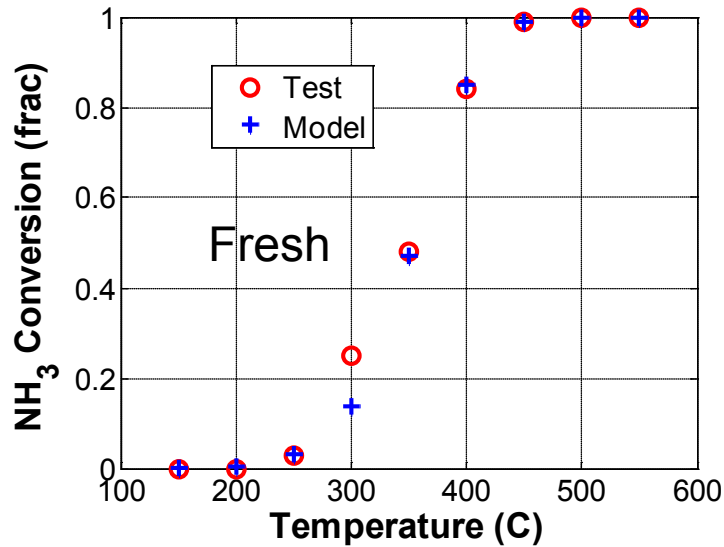


- ▶ A fifth reaction (same for both sites) was also used under anaerobic conditions of storage experiments to describe an observed loss of NH₃

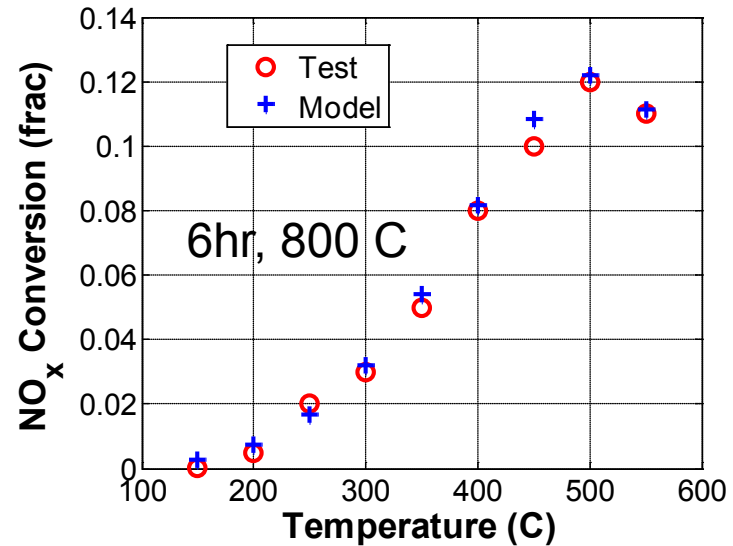
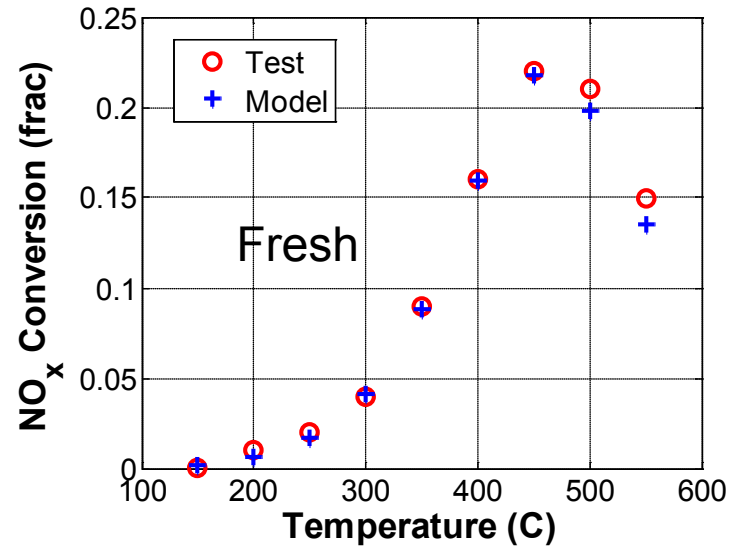


Kinetic Models for NH_3 and NO Oxidation

NH_3 Oxidation

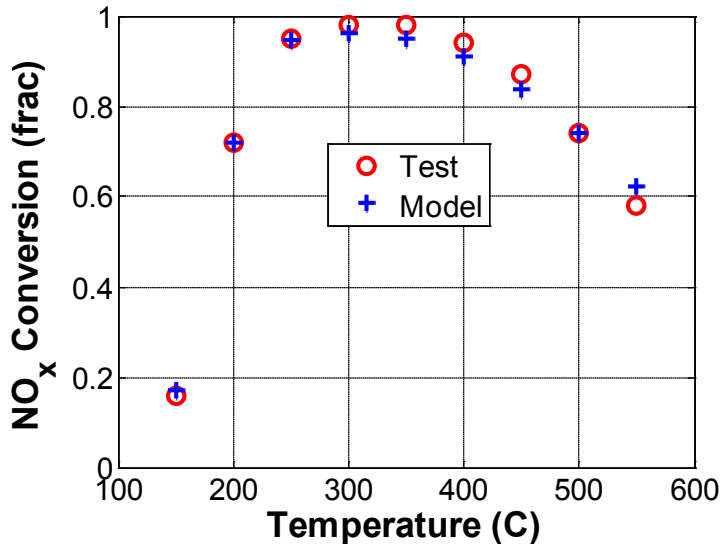


NO Oxidation

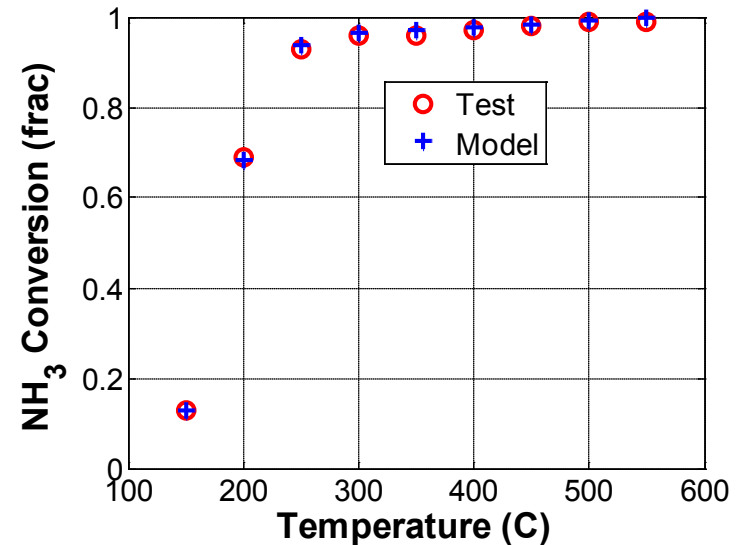
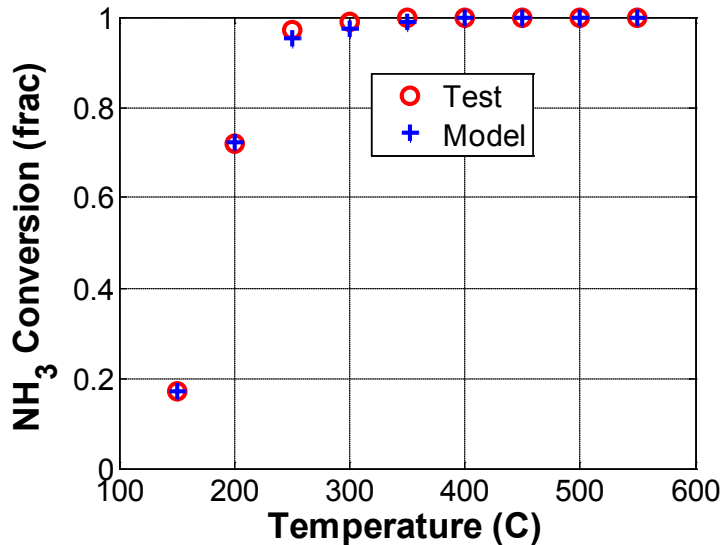
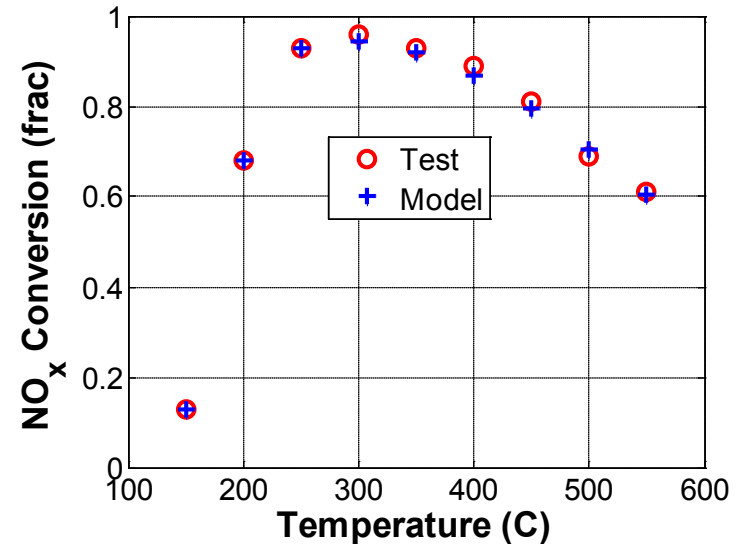


Kinetic Models for Standard SCR Reaction

Fresh



Aged 6hr, 800 C



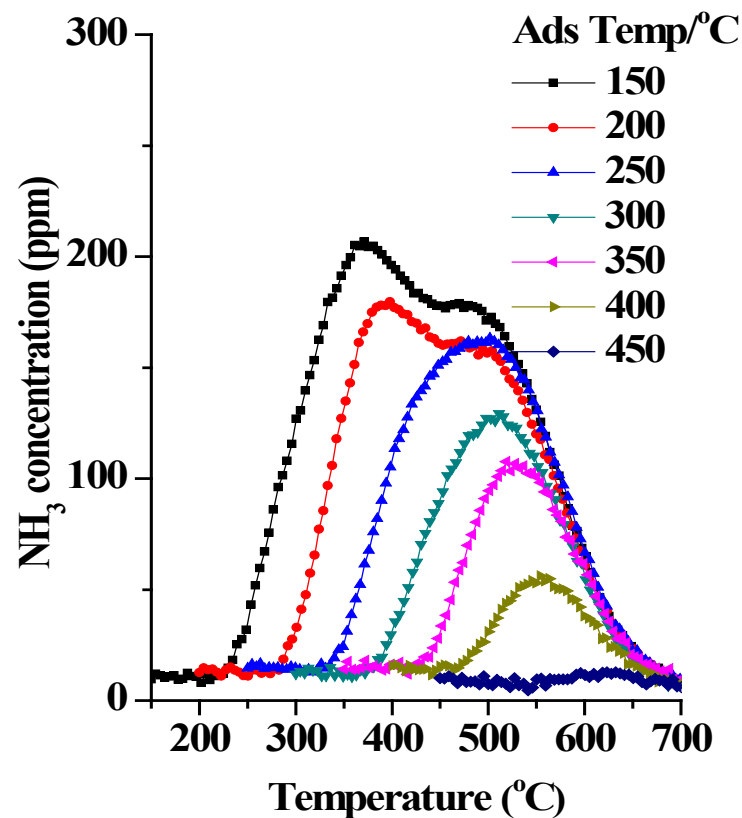
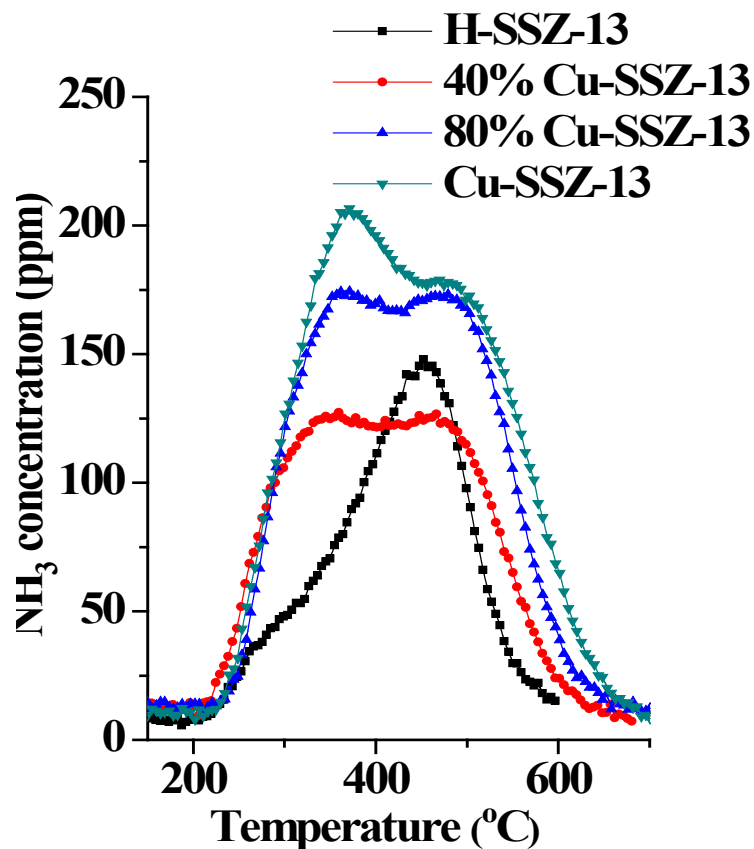
Modeling has identified specific questions currently being addressed with experiments

- ▶ What are the nature of sites/surfaces available for NH_3 storage?
 - Bronsted acid
 - Lewis acid
 - physi-sorption
 - metal?
- ▶ How is NH_3 distributed among these sites at various points of time during SCR operation?
- ▶ Which of the sites have coverage-dependent desorption kinetics, and how best is that dependence modeled? Tempkin isotherms?
- ▶ Are there some sites that store NH_3 but serve no catalytic function?
 - If so, must NH_3 be released from these sites and re-absorbed on active sites in order to take part in reactions?
- ▶ How does the distribution of storage sites change during hydro-thermal aging?

Experimental Studies of State-of-the-art Cu SCR Catalysts

- ▶ Both Cu-SSZ-13 and Cu-SAPO-34 catalysts synthesized and studied at PNNL – **these model catalysts allow for fundamental studies of their catalytic and material properties**
 - Both CHA zeolites synthesized by published hydrothermal methods.
 - Cu loaded into SSZ-13 via aqueous ion exchange.
 - *Many methods explored to incorporate Cu into SAPO-34. Very difficult to obtain reproducible model catalysts but significant progress has been made.*
- ▶ New results obtained this past year have included:
 - Characterization of the Cu species as a function of Cu loading by temperature-programmed reduction (TPR) and EPR spectroscopy measurements (scientific journal manuscripts have been published – see list below and backup slides)
 - Ammonia storage sites determined as a function of Cu loading, and comparative reactivity of different ammonia sites assessed.
 - NO_x SCR and NH₃ oxidation performance as a function of Cu loading measured under kinetically-controlled conditions (see publication list)
 - Our latest results have been documented this year in 7 publications, as well as 10 presentations (5 invited) at scientific conferences.
 - Part of the team (co-PI) on a newly NSF/DOE-funded university-based project.

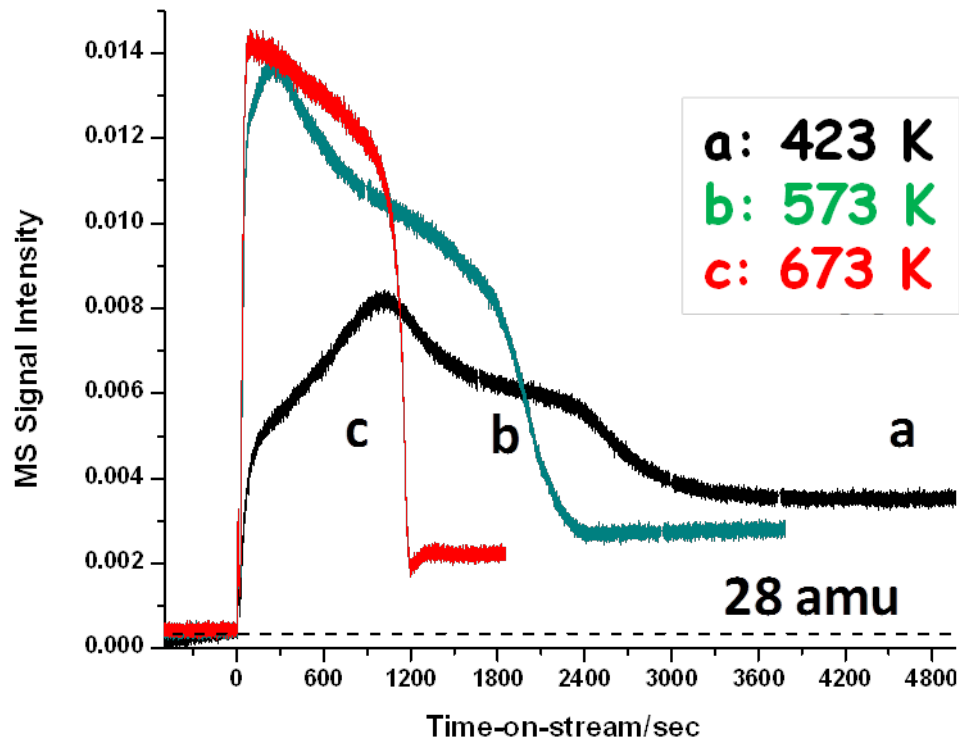
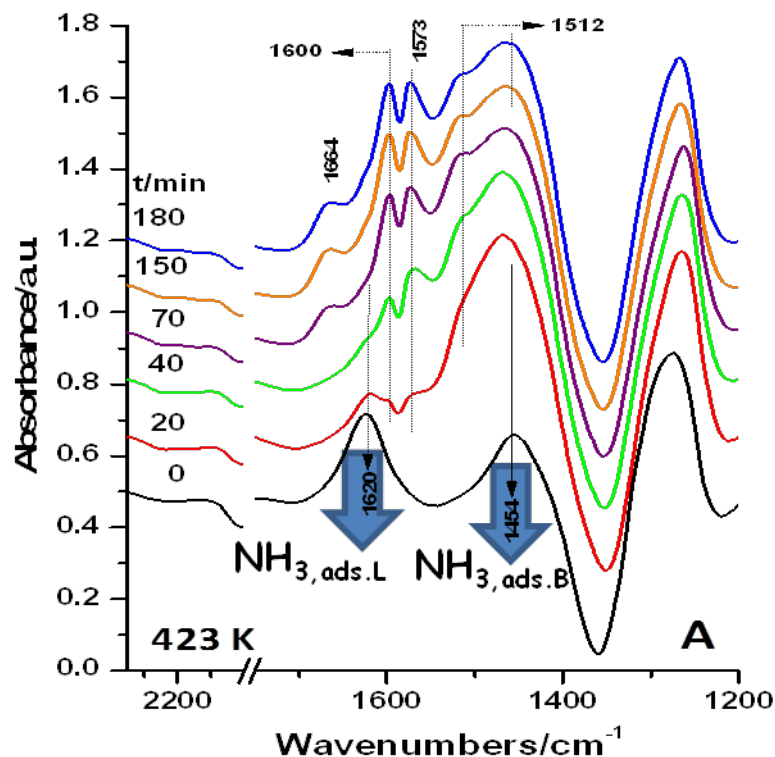
TPD Experiments Probe the Nature of Ammonia Storage Sites in Cu-SSZ-13 Catalysts



- Only “Brönsted” are present on H-SSZ-13
- “Lewis” acidic sites are formed as Cu is incorporated.
- Either Brönsted sites are filled first or ammonia migrates to most stable sites before desorbing.

'Operando' Studies Show the Much Higher Reactivity of Lewis-bound Ammonia on Cu-Sites

Oxidation of adsorbed NH_3 with NO_2 : DRIFTS and MS

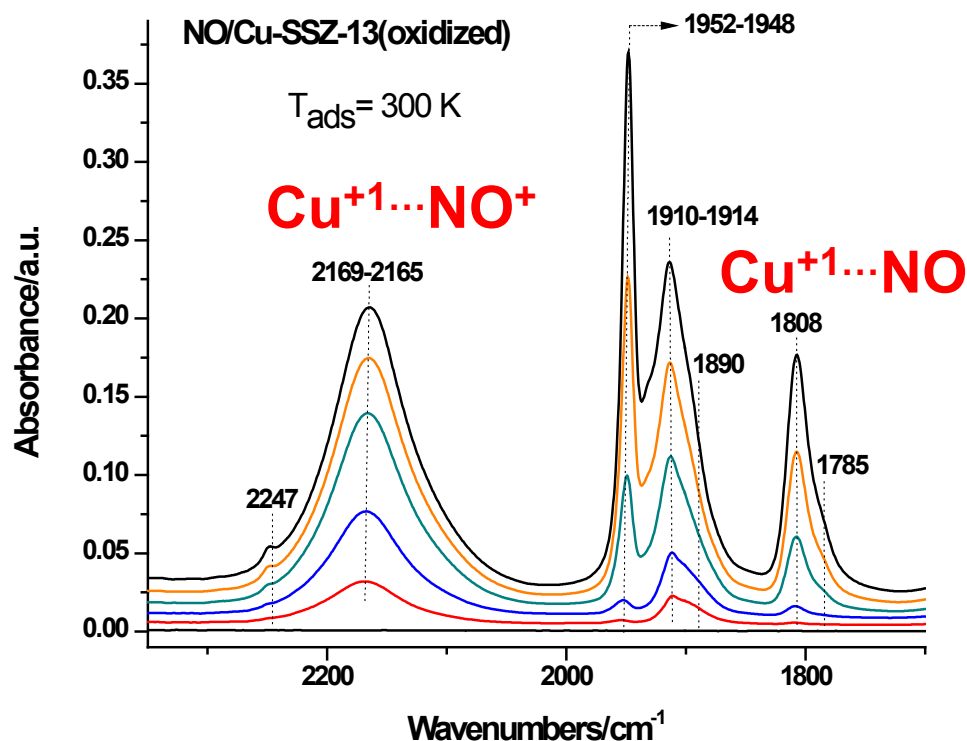


- FTIR peak associated with Cu-bound NH_3 is removed rapidly, while NH_3 adsorbed on "Brönsted"-sites only very slowly decays.
- Product (N_2) formation followed simultaneously with mass spectrometry.

H Zhu, JH Kwak, CHF Peden, J Szanyi,
Catalysis Today 205 (2013) 16-23.

NO Adsorption on oxidized Cu/SSZ-13

Cu⁺²...NO

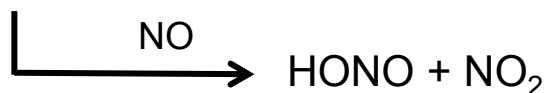
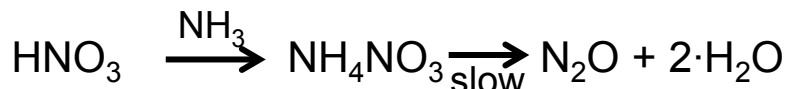
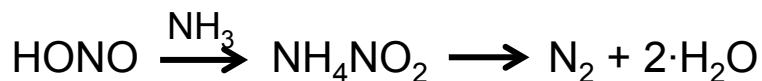
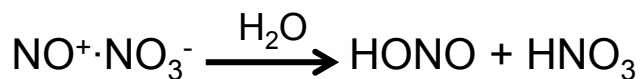
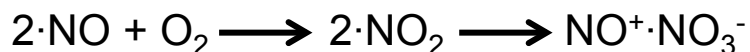


- Peaks between ~ 1850 and $\sim 2000 \text{ cm}^{-1}$ can be assigned to NO adsorbed on Cu⁺².
- Unusually high wavenumber ($\sim 2165 \text{ cm}^{-1}$) peak is assigned to an NO⁺ Species.
- Cu⁺¹ adsorbed NO species forms after NO⁺.
 - Some Cu⁺² reduced by NO?
 - NO then chemisorbs on Cu⁺¹?
- No evidence for nitrate species (NO₃⁻) upon adsorption of NO even in the presence of oxygen.

J Szanyi, JH Kwak, H Zhu, CHF Peden,
PCCP 15 (2013) 2368-2380.

Mechanistic Implications

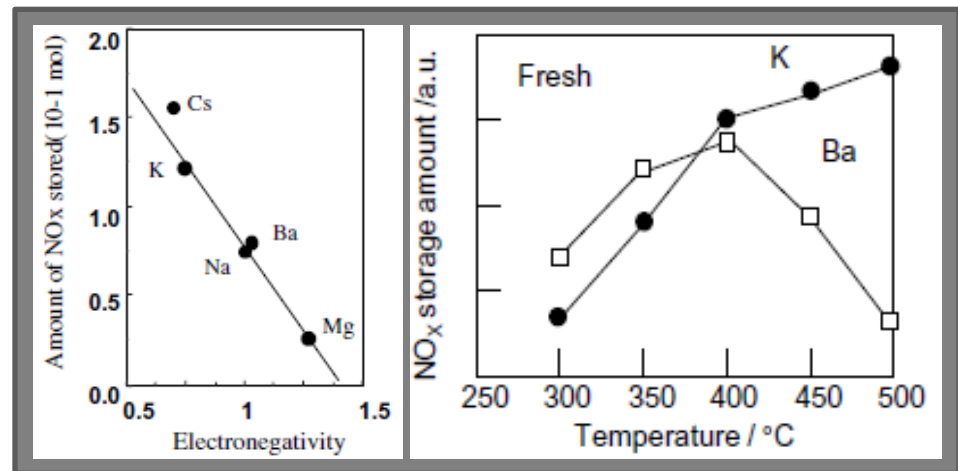
Proposed Elementary Steps



- ❑ Nitrates and NO^+ are proposed products of NO_2 disproportionation.
- ❑ NO^+ reaction with NH_3 leads to N_2 production.
- ❑ Nitrates + NH_3 results in N_2O formation (*not observed for Cu/SSZ-13*).
- ❑ Formation of NO^+ without nitrates for Cu/SSZ-13 can rationalize selectivity.
- ❑ Cu+1 observed during SCR reaction with XANES – Ribeiro and coworkers, Cat. Today 184 (2012) 129-144.

NO_x Storage-Reduction (NSR) Catalysts {aka. LNT}

Conventional Ba-based NSRs operate best between 350 and 400°C; K-based NSRs show potentially much better performance at higher temperatures

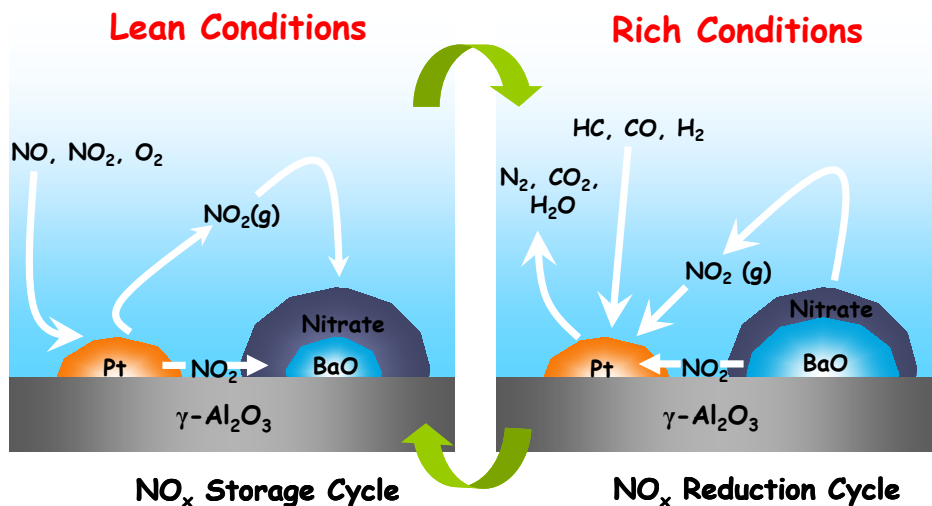


Toyota: Top Catal. 28(2004)151

Approach

- Higher temperature NO_x reduction performance required for:

- Difficult to meet “not to exceed” regulations during desulfations
- Possible use of NSRs for lean-gasoline applications



- PNNL/Cummins/JM CRADA has focused on degradation of possible materials for next-generation high temperature NSRs.
- A relatively small effort in our CLEERS program is addressing more fundamental issues of these potential new NSR materials related to composition, morphology, and chemical reaction kinetics and mechanisms.
- For these studies, PNNL has prepared a range of materials based on literature and prior CLEERS work at PNNL.
- 2 scientific journal publications and 2 conference presentations this year.

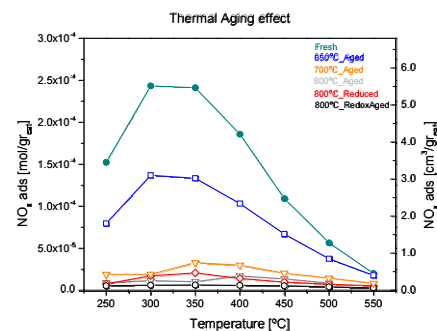
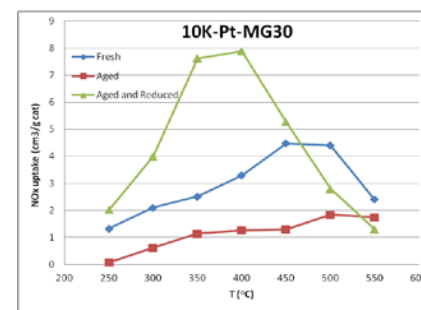
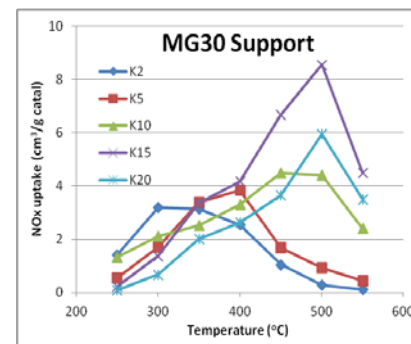
Focus on K-Based NSR Materials

- ▶ K/Pt/Al₂O₃ (2%, 5%, 10%, 15%, 20%, weight):
 - **Pt/Al₂O₃** (1%): Impregnation of Al₂O₃ (150 m²/g) with Pt(NH₃)₄(NO₃)₂, 500°C calcination for 4hrs
 - **K loading**: Impregnation of Pt/Al₂O₃ with K₂CO₃ of different K loadings, 600°C calcination for 4hrs
- ▶ K/Pt/MgAlO_x (2%, 5%, 10%, 15%, 20%, weight):
 - **MgAlO_x Support** (Pural MG30: Mg/Al=0.6): Calcination at 600°C for 4hrs
 - **K and Pt loading**: as with the alumina-supported catalysts
- ▶ K/Pt/TiO₂ (2%, 5%, 10%, 15%, 20%, weight):
 - **TiO₂ Supports** (P-25, Hombicat)
 - **K and Pt loading**: as with the alumina-supported catalysts
- ▶ NO_x storage performance testing and catalyst characterization by KNO₃-TPD (decomposition), NO_x TPD (after NO₂ adsorption), XRD and TEM
- ▶ Aging and sulfur tolerance have been studied as part of Cummins CRADA.

Primary Focus has been Issues of K Mobility and Reactivity

Results obtained this year have included:

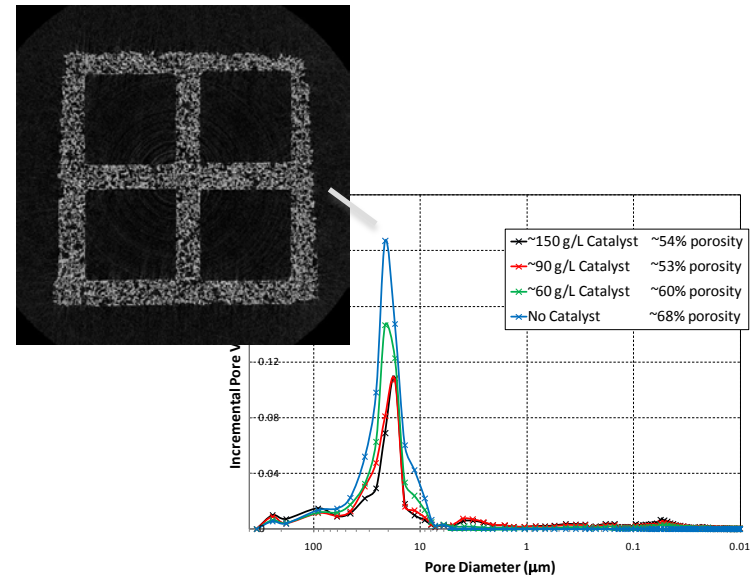
- ▶ Unusual optimum performance with K loading observed on all support materials.
- ▶ XRD indicates K-nitrate melting before decomposition; likely forming a highly mobile molten salt.
- ▶ On Mg-aluminate supports, performance can be restored after high temperature deactivation.
- ▶ Prior literature indicated titania as a promising support material for K-based NSR catalysts. **However**, we find that titania-supported catalysts are permanently deactivated during thermal treatments due to formation of potassium-titanates (evidenced in XRD).



Diesel Particulate Filter

Exhaust Particulates and Filter Technology

- ▶ Majority of FY13 exhaust particulate activity is planned for the second half of the year
- ▶ Cooperative experiments at ORNL will apply advanced aerosol characterization techniques used previously with single-cylinder lab engines to a production lean SIDI vehicle (2.0L BMW)
 - New engine control system at ORNL will allow detailed exploration of operating parameter space
 - SPLAT-II instrument combined with other methods provides detailed information on size, shape and composition of various families of particles in exhaust
- ▶ A new set of high-resolution micro X-Ray CT data has been obtained for filter samples with various loadings of a current SCR catalyst produced by a commercial supplier
 - Analysis of images will attempt to determine how the catalyst is distributed throughout the porous wall at different loadings
 - Affects of catalyst loading on 3-D pore space relevant to ΔP and filtration performance will be examined
 - Lattice-Boltzmann simulations will be used to evaluate accessibility of catalyst to flowing exhaust
 - Characteristic dimensions of pores will be compared to more readily available metrics, such as mercury porosimetry data



Conclusion & Future Work

Conclusions

► SCR

- A new two-site SCR model of a current commercial Cu-CHA catalyst shows promise for better prediction of NH₃ storage and NO_x reduction as the catalyst ages.
- Ammonia storage sites on Cu-SSZ-13 zeolites have been characterized with temperature-programmed desorption and FTIR experiments. NH₃ adsorbed on Cu sites are by far the most reactive.
- Recent 'operando' FTIR studies are providing important information concerning the mechanism of the selective catalytic reduction of NO_x with NH₃.

► NSR

- Unlike Ba-based NSRs, the temperature for optimum performance of K-based NSR catalysts show a large and unexpected dependence on loading on all support materials (Al₂O₃, MgAl₂O₄, TiO₂) studied to date.
- While MgAl₂O₄-supported materials can be regenerated after high temperature deactivation, TiO₂-supported ones are permanently degraded due to formation of potassium-titanate phases.

► DPF

- Have obtained high resolution, three dimensional micro-CT images of a current high-porosity filter substrate professionally coated with various loadings of a state-of-the-art SCR catalyst and begun detailed analysis.

Future Work

- ▶ SCR
 - Tune kinetic parameters for reactions involving NO₂ in the two-site SCR model.
 - Validate SCR model with additional aging states and propose an aging model for the Cu-CHA catalyst.
 - Seek to simplify the two-site model so that it adequately describes device performance with the bare minimum of reactions and tunable parameters.
 - Experimentally address the continuing fundamental issues being identified in modeling studies.
 - In collaboration with collaborators on new NSF/DOE-funded program, probe the nature and stability of the active Cu species in the CHA-based catalysts, especially for SAPO-34 zeolite-based catalysts.
 - Continue studies of the reaction mechanism for these catalysts; low NO oxidation activities for these catalysts suggest a fundamentally different chemical process.
- ▶ NSR
 - Detailed catalyst characterization to determine origins of optimum high temperature performance of K-based NSRs.
 - Continue studies of ways to control the mobility of K in this class of NSR catalysts which is a significant concern for their practical application.
- ▶ PF
 - Seek to identify key length scales and pore features associated with backpressure and filtration performance and examine how they are altered by catalyst coatings in multi-function filter devices
 - Conduct cooperative experiments at ORNL to help characterize particulates from an advanced lean-burn gasoline direct injection vehicle
 - Continue development of improved pore-scale and device-scale filtration models

Acknowledgements

- ▶ PNNL

Andrea Strzelec (now at TA&M), Maruthi Devarakonda (now at GE), Shelley Carlson, Laura Righini, Gary Maupin, Alla Zelenyuk

- ▶ ORNL

Stuart Daw, Jim Parks, Josh Pihl, and support from the ORNL team

- ▶ Academia

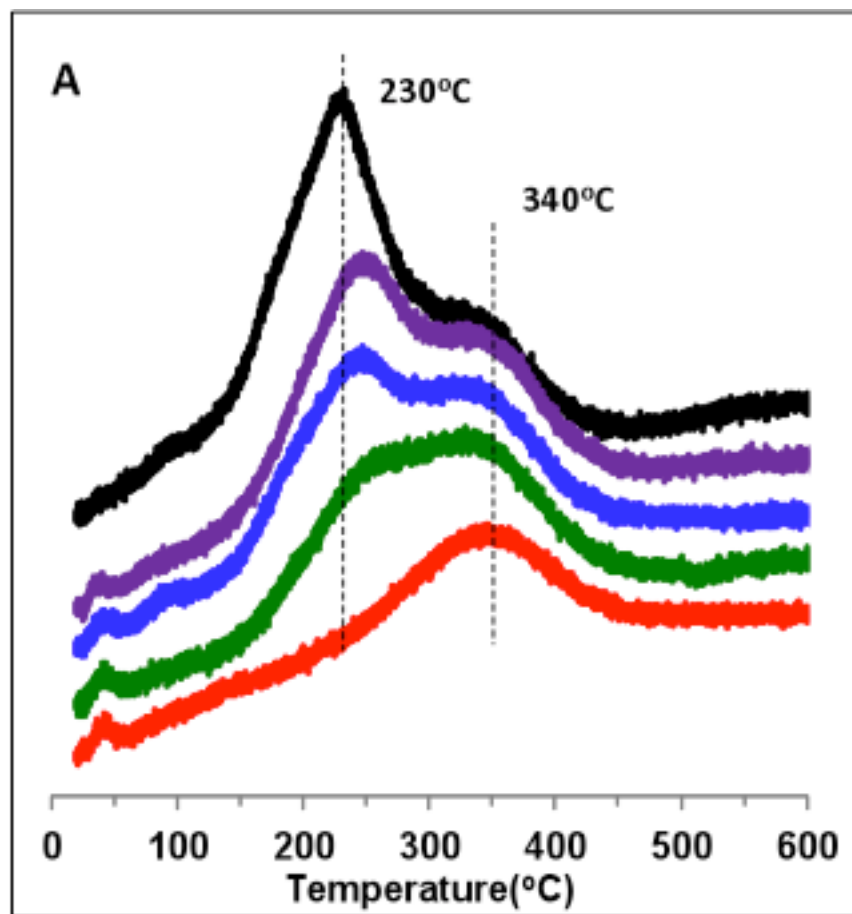
Randy Vander Wal (Penn State)

- ▶ DOE Vehicle Technologies Program

Gurpreet Singh and Ken Howden

Technical Back-up Slides

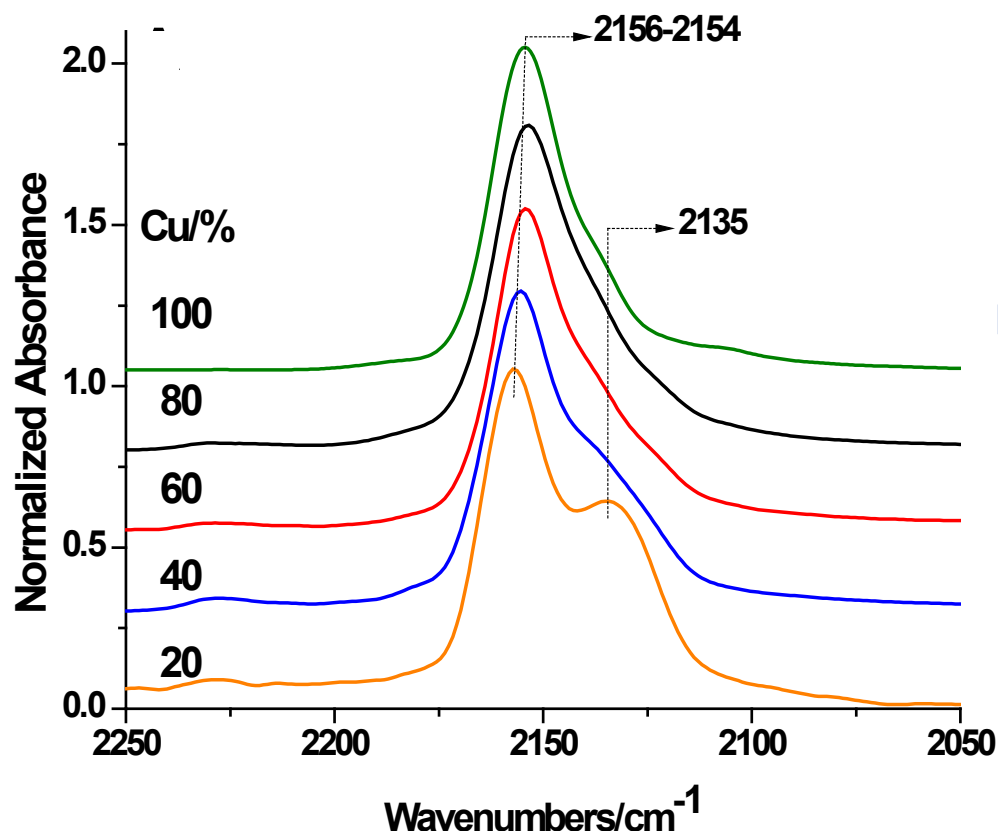
Effect of Cu Loading on the Reduction of Cu Species in Cu-SSZ-13 Zeolites Catalysts



- ▶ At low loading, only a single H₂ TPR reduction peak at ~340 °C.
- ▶ At higher loadings, a second TPR peak appears at ~230 °C, which monotonically increases in size with increasing Cu loading.
- ▶ However, recent literature from Lobo and coworkers has suggested a single Cu site in SSZ-13 CHA zeolite.
- ▶ Our TPR results are consistent with our recent FTIR and EPR spectroscopic measurements (see following slides).

JH Kwak, H Zhu, JH Lee, CHF Peden, J Szanyi,
Chemical Communications 48 (2012) 4758.

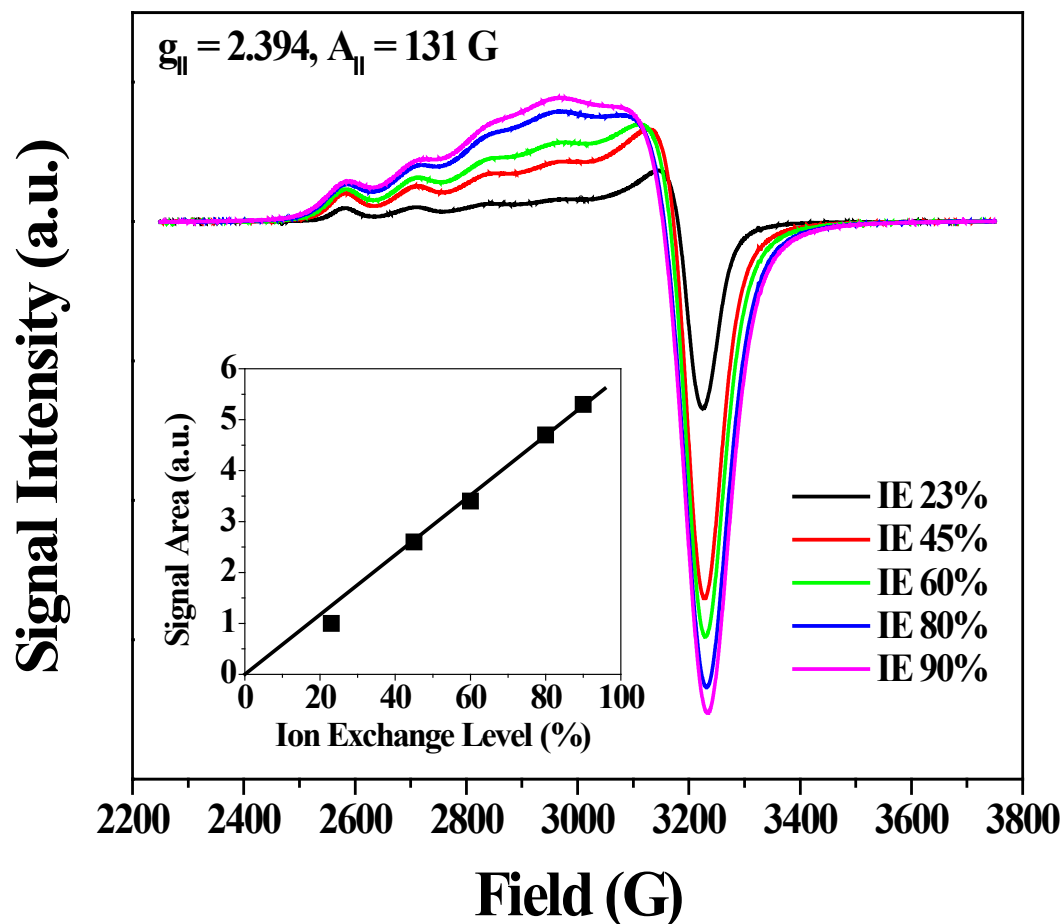
CO Adsorption on Cu/SSZ-13



- FT-IR of CO adsorption on Cu/SSZ-13 shows two CO-Cu⁺ vibrational peaks at ~2155 and ~2135 cm⁻¹.
- Change in relative intensities of the peaks with respect to Cu ion exchange levels suggest:
 1. two different Cu species in Cu-SSZ-13; and
 2. relative distribution of these species is dependent of Cu loading levels.

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Low Temperature EPR of Cu(various)/SSZ-13 Catalysts

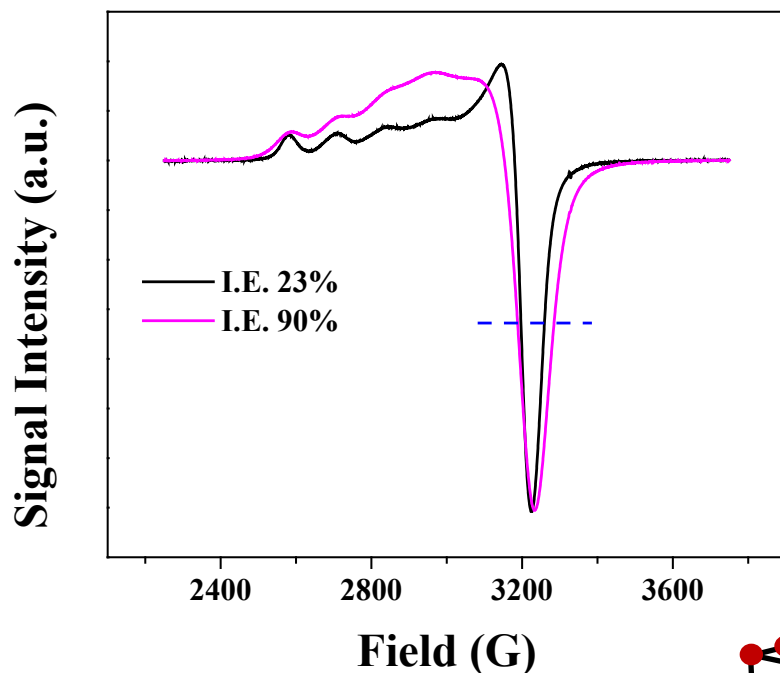


- Done at 155 K to freeze Cu^{2+} in place.
- Up to IE of 90%, linear relationship between signal intensity and Cu content. Suggests all Cu^{2+} are EPR active, i.e., all Cu^{2+} are isolated monomers.
- EPR parameters consistent with Cu in octahedral coordination.

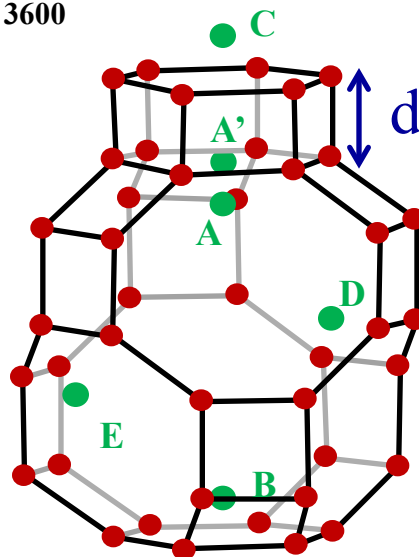
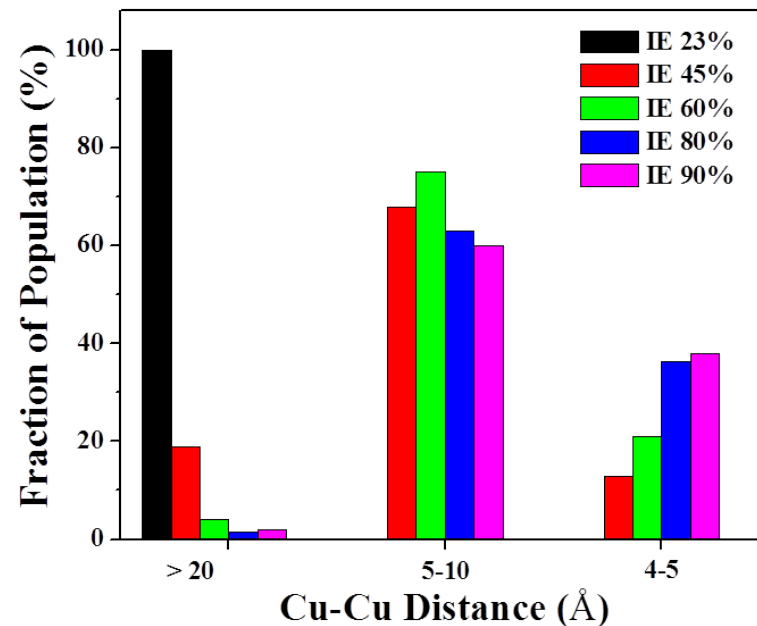
Line broadening is due to dipole-dipole interactions which are dependent on Cu-Cu distances. We use this to estimate these Cu-Cu distance.

Active Sites & Locations: EPR

"Normalized" EPR



Cu-Cu distance Estimation



$$\Delta E = g\mu_B H_0$$

$$\Delta E_{dd} = \frac{\mu_0}{4\pi} g^2 \mu_B^2 \frac{1}{r^3}$$

$$a = b = 13.719 \text{ Å}$$

$$c = 14.953 \text{ Å}$$

$$d = 3.8 \text{ Å}$$